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REMARKS

Upon entry of the above amendments, claims 1-4, 7, 8 and 10-45 will be pending. Applicants propose amendment of claim 1 to incorporate the features of claims 5 and 6. Accordingly, claims 5 and 6 are canceled, and claim 7 is amended to change its dependency from claim 5. Entry of the amendments after final rejection does not raise new issues since the limitations added to claim 1 were under consideration.

Claims 1-8, 10-32, 39 and 40 were rejected under 35 USC §103(a) as being unpatentable over Altieri. This rejection is respectfully traversed.

Altieri requires its starch material to be a high amylose starch, i.e., one containing at least 45% by weight of amylose (see column 4, lines 4-8, for example).

Claim 1 has been amended to specify that the starch is a natural starch derived from one of potato, wheat, maize or tapioca starch, as previously set forth in claim 6. These starches have an amylose content well below the high amylose starches of Altieri. Indeed, Altieri even distinguishes over such starches as noted at column 4, lines 11-23. Thus, Altieri teaches away from the claimed invention. There is no suggestion or teaching provided by Altieri which would have motivated one of ordinary skill art to employ a starch having an amylose content less than the 45% by weight required by Altieri.

Attached is a table taken from Starch Chemistry and Technology, 2nd Edition, showing the amylose content of starches, for the Examiner's reference.

In addition to the above patentable difference of the present invention over Altieri, claim 1 also requires a specific intrinsic viscosity which is not taught by Altieri.


Accordingly, the claimed invention distinguishes over the cited and defines patentable subject matter. Favorable reconsideration is earnestly solicited.

Should the Examiner deem that any further action by applicants would be desirable to place the application in better condition for allowance, the Examiner is encouraged to telephone applicants' undersigned attorney.

In the event that this paper is not timely filed, Applicants respectfully petition for an appropriate extension of time. Please charge any fees for such an extension of time and any other fees which may be due with respect to this paper, to Deposit Account No. 50-2866.

Respectfully submitted,

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Attachments: Starch Chemistry and Technology (pages 250-253)
Petition for Extension of Time
Notice of Appeal

SGA/arf

Atty. Docket No. **030229**
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STARCH

Chemistry and Technology

SECOND EDITION

Edited by

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STARCH

Chemistry and Technology

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SECOND
EDITION

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29439

All starches examined by Whistler and Doane (15) contained an intermediate fraction. The intermediate fraction comprises 4-9% of normal corn starch (6, 9, 16-18) and may be considered amylopectin with a lower degree of branching (see Chap. VI). Some of the amylose molecules may be slightly branched with infrequent α -D-(1 \rightarrow 6) linkages that do not significantly affect the molecule's physical properties (19). Greenwood (20) thinks that most amylose contains a small degree of branching (see Chap. VI).

2. Comparison of Amylose and Cellulose

Isotactic amylose and syndiotactic cellulose have the same empirical formula, but in cellulose the D-glucopyranosyl units are linked in the β -D-(1 \rightarrow 4) configuration with the D-glucopyranosyl units alternating in 180° rotation.

Cellulose forms strong microcrystalline regions called crystallites. Its β -D-(1 \rightarrow 4) glucosidic linkages permit an extended chain enabling molecular alignment in crystallites and provides reduced solubility. Only through solvents or formation of derivatives that disrupt hydrogen bonds is cellulose dispersible. The uniform linear-chain nature of amylose polymers permits them to crystallize from solution as well as in the semi-solid state in films and coatings in a manner similar to that of other linear polymers such as poly(propylene) and cellulose. The α -D-(1 \rightarrow 4) bonds of amylose give the linear chains a less extended configuration. The resulting more poorly crystallized amylose can be solubilized in water alone when it is heated for 1-2 min at temperatures above 124°. On cooling, however, the amylose readily crystallizes and precipitates.

3. Amylopectin Molecule (see also Chapter VI)

The branched structure of amylopectin provides greater solution stability than is possessed by amylose. With time and low temperatures or very high concentrations, however, amylopectin can also partially crystallize. The crystalline nature of amylopectin is observed in all starch granules, even those containing only branched amylopectin such as waxy corn (21, Chapter VII). Leaching experiments which release amylose preferentially from the granule imply that amylose is not extensively associated within the crystalline regions of the native granule.

Amylopectin is heterogeneous with respect to molecular weight distribution and very likely with respect to frequency of branching (22). In corn starch, branches occur an average of once for every 26 α -D-glucopyranosyl units through α -D-(1 \rightarrow 6) linkages (Chapter VI). Branches may be close together or be over 40 sugar units apart. The inner chain segments seem to be shorter and more closely spaced, giving the molecule a dense core (23, 24). Some amylopectin molecules may have very long outer branches (15). There is some evidence that a

small amount of branching occurs through α -D-(1 \rightarrow 3) linkages (25). Fractions which are more highly branched than normal amylopectin are also known (26-29). The mean variation in branch length is not known. The average chain length and the β -amylosyl units limit vary with increase in maturity of the plant (20).

4. Starch from Various Plants (see also Chapter III)

The amylose content of a number of starches is shown in Table I (10, 13, 30-37). Starches from different sources, such as wrinkled pea, normal corn, and waxy maize, contain widely different amounts of amylose. Most native starches contain 20-30% by weight of amylose. One variety of wrinkled pea contains a starch having 66% amylose. The ratio of amylose to amylopectin and/or the linearity and frequency of branching can be genetically controlled (34). Certain varieties of hybrid corn, such as Amylomaisze, have starch with more than 80%

Table I
Amylose Content of Starches

Starch	Amylose (%)	Reference
Acorn	24	30
Apple	19	13
Arrowroot	20.5	31
Banana	16	13
Barley	22	13
Waxy	0	32
Elder lily	34	32
Elm, sapwood	21.5	37
Irish tuber	27	31
Corn (Zea mays)	28	13
Hybrid amyloseless Class V	52	13
Hybrid amyloseless Class VII	70-75	10
Hybrid waxy maize	0.8	31
Oat	27	13
Pea	35	13
Smooth	66	13
Wrinkled	15.7	31
Manioc	11	13
Peanut	20	31
Potato	18.5	31
Rice	0	32
Waxy	25.8	31
Sago	0	32
Sorghum, waxy	17.8	31
Sweet potato	16.7	31
Tapioca	26	13
Wheat		

anylose (35) when measured by iodine binding capacity (32). Waxy maize, waxy sorghum, waxy barley, and waxy rice starches contain no anylose.

5. Considerations of Starch Structure

To disperse and fractionate starch molecules that might possess outer branches of up to 12,000 α -D-glucopyranosyl units, heat, shear, and complex formation have been used, but these methods may cleave the long outer branches, especially if high concentrations of starch are used. Therefore, separation of starch into two or more fractions is not conclusive evidence that the polymers were originally present as a mixture in the starch granule (36).

The occurrence of a linear α -D-(1 \rightarrow 4)-linked anylose and a branched amylopectin with about 4% α -D-(1 \rightarrow 6) linkages as two separate natural polymers is not universally accepted (8). Potze (8) points out that fractionation procedures are usually preceded by such rigorous dissolution methods that two polymers could be formed from pre-existing large molecules by debranching. Badenhuizen (37) supports arguments for the existence of only one constituent substance in starch. Bauer and Pecsú (38) conclude that starch anylose and amylopectin are bound together to form native starch molecules. Langlois and Wagoner (36) believe that the fractionation of starch into linear and branched components is not proof that a mixture exists in the granule. Richardson and workers (39) conclude that the differences in the relative proportions of chemically defined "anylose" and "amylopectin" observed by various workers owe partly to differences in pretreatments and in separation methods.

Greenwood (20) states that, although there is a vast amount of evidence for the heterogeneous character of starch, the starch granule may be a giant molecule and such a unitarian concept has to be seriously considered. Banks and Greenwood (40) claim that, the more that is known about starch, the more it is realized that few generalizations about its structure and behavior are possible. They conclude that the biosynthetic routes and the reasons for deposition of a multiplicity of polysaccharide structures remain matters of conjecture (41).

Exclusion chromatography (42, 43) produces fractions that raise the possibility that native starch may be, not a mixture of branched and linear molecules of D-glucopyranosyl units, but a mixture of covalently bound branched molecules having some extremely long chains, a broad degree of branching, and broad molecular weight distributions.

Regardless of how anylose occurs in the starch granule, methods have been developed to separate it from the branched amylopectin; and some methods have been used commercially (7, 44). The present high cost of energy required for fractionation of starch makes commercial fractionation less attractive, (45) especially because developed genetic hybrids of corn provide starches that function commercially as well as commercial anylose (35, 46) and amylopectin (47).

Except for exclusion chromatography, most analytical methods for starch fractionation are based on differential solubility. Free anylose and low-molecular-weight amylopectin can be leached from the granule, or the granule can be dispersed and the less soluble anylose component complexed or precipitated. Refined techniques can subfractionate anylose into different molecular weight groups.

II. MOLECULAR WEIGHT OF FRACTIONS

Standard methods for determination of polymer molecular weight (48) can be used. The average molecular weights (\bar{M}_n = number average, \bar{M}_w = weight average, and \bar{M}_v = viscosity average) are defined by the equations:

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \quad (1)$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \sum w_i M_i \quad (2)$$

$$\bar{M}_v = \left[\frac{\sum n_i M_i^{(1+\alpha)}}{\sum n_i M_i} \right]^{1/\alpha} \quad (3)$$

where n_i = number of each molecule possessing a molecular weight M_i ; w_i = weight fraction of each molecule possessing a molecular weight M_i ; and α = constant for each type of polymer-solvent system, usually in the range 0.5–1.0.

The number-average molecular weight is the total weight of sample divided by the total number of moles. Any colligative method, such as osmotic pressure or end-group analysis, can give the number of solute molecules.

Weight-average molecular weight, \bar{M}_w , is often determined by light scattering. For heterogeneous samples, \bar{M}_w is always $>\bar{M}_n$.

Viscosity-average molecular weight becomes equal to \bar{M}_w if $\alpha = 1$.

Small molecules affect the number-average molecular weight to a greater extent than do large molecules. The number-average molecular weight loses significance for broad molecular weight distributions, since it is not sensitive to larger molecules. The weight-average molecular weight is more sensitive to the contributions of large molecules and not as sensitive to small molecules. Thus, both averages have shortcomings for broad molecular weight distributions and are best employed for molecular characterization of narrow molecular weight fractions. The extent of the molecular weight distribution can be indicated by the ratio of \bar{M}_w/\bar{M}_n . For fractions of narrow molecular weight distributions, the ratio can be close to 1.

The following two examples show how average degree of polymerization values can vary. A mixture of molecules composed of α -D-glucopyranosyl units and with degrees of polymerization of 1, 10, 100, 1000, and 10,000 have a